

FWP and possible subtask under FWP:

SSRL Materials Research, Subtask 1: Complex Materials

FWP Number: SCW0035

Program Scope:

(1) Conduct cutting-edge research using spectroscopy and scattering techniques, by correlating information gained from single particle (photoemission) and two particle (neutron and x-ray scattering) response functions. (2) Provide scientific impetus for developing state-of-the art photoemission capabilities at DOE's synchrotron sources (SSRL and ALS). These capabilities have become national resources for many experimental groups. (3) Develop crystal growth and characterization capabilities. These capabilities, and the materials generated, have enabled extensive collaborations, nationally and internationally. (4) Conduct related theoretical investigations, broadly defined. (5) Develop human resources by training and educating students and post-docs.

Major Program Achievements (over duration of support):

Electronic and magnetic structure of electron doped superconductors: We have performed systematic studies of the electronic and magnetic properties of the electron-doped $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ family of superconductors. We have the following novel results: i) Photoemission experiment provided first evidence that the Mott insulating gap is not a direct gap, thus revealing an electronic structure feature that is important to understand a range of novel properties. ii) The electronic structure evolution from a Mott insulator to a superconductor is a highly non-trivial process: the electrons first form Fermi surface pockets near the non-magnetic Brillouin zone boundary, then pockets near the magnetic zone boundary, and eventually the normal behavior predicted by conventional theories. iii) We discovered the Fermi surface hop spot caused by the (π,π) antiferromagnetic spin scattering, a phenomenon predicted to be important to the physics of cuprates but never observed. iv) Inelastic x-ray scattering reveals the doping dependence of the phonon anomaly, providing evidence for a strong electron-phonon coupling. v) Neutron scattering yields information on spin correlations and magnetic moments, allowing quantitative comparison with numerics and emerging theory (based on prior ARPES work). vi) X-ray and neutron diffraction reveals existence of a minority chemical phase in oxygen-reduced $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. Magnetic field experiments demonstrate that paramagnetic effects from this secondary phase have been misinterpreted by others as a quantum phase transition from a superconducting to an antiferromagnetic state. vii) Neutron scattering on $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ under magnetic field revealed the nature of the normal state that was masked by superconductivity.

Discovery of an pseudogap analogue in ferromagnetic manganites: We have discovered a polaron driven pseudogap in the layered ferromagnetic $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, revealing the importance of the interactions between electrons and lattice vibrations to colossal magnetoresistance. This result also brings to light unexpected similarities between the electronic structures of manganites and high temperature superconductors. We have also studied the structural and magnetic properties of other novel manganites such as $\text{La}_{1-x}\text{Sr}_{1+2x}\text{MnO}_4$ and $\text{La}_{3-x}\text{Ca}_x\text{MnO}_3$.

Program Impact:

The comprehensive approach of materials synthesis, measurement and theory has been the key to enabling higher productivity over the simple sum of the individual efforts. The unique experimental capabilities at the DOE facilities enabled experiments not possible otherwise. Our discoveries have significantly impacted the field because it identifies the key microscopic ingredients in these novel materials.

Interactions:

UCLA, U. of Tokyo, U. of Wuerzburg, Tohoku U., UC Santa Cruz, ANL, U. of Leiden (Netherlands), Scienta Inc. (Sweden), Columbia U., NIST, AMES Labs, U. of Illinois, ALS-LBNL, BNL., Elettra, Kyoto Univ., BENSC (Germany), U. of British Columbia, ISTECS-Superconductivity Lab. (Japan), ANL, Bell Labs., U. of Toronto, LLNL, NRC, U. Pierre de Marie Curie, Chalk River (Canada), LLB (France), ORNL.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Over 50 Invited Talks at international conferences since 2003; William Spicer Award (Armitage), McMillan Award (Armitage), Shirley Award (Zhou).

Personnel Commitments for FY2005 to Nearest +/- 10%:

Z.-X. Shen 5%, S. Doniach 10%, M. Greven 10 %, R. Laughlin 0%

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$495K **FY04:** \$495K **FY05:** \$495K

FWP and possible subtask under FWP:

SSRL Materials Research, Subtask 2: Magnetic Materials

FWP Number: SCW0035

Program Scope:

This program is aimed at using the unique capabilities of x-rays and ultrafast electron beams to address forefront issues in the area of magnetic materials and phenomena. The present research program has three components.

1. The determination of the magnetic structure of thin films and interfaces in magnetic multilayers by x-ray spectroscopy and microscopy. This is of great importance because all novel magnetic devices are based on spin transport across interfaces between thin layers, and the interface structure determines the transport.
2. Development of lensless magnetic imaging by means of coherent x-ray scattering techniques. One of the exciting applications of future x-ray lasers consists of single-shot ultrafast imaging. Our goal is to take snapshots of ultrafast magnetic processes that are not reversible.
3. Exploration of ultrafast magnetic switching with the unique magnetic field pulses of the SLAC LINAC. Today's magnetic technology is limited to response times of about 1 nanosecond. This program explores the limits in magnetic switching speeds down to unprecedented time scales.

Major Program Achievements (over duration of support):

The achievements are listed separately for the three areas above.

1. We have used x-ray photoemission electron microscopy to study a variety of magnetic multilayer systems. In a series of high profile publications we have solved the origin of "exchange bias". The latest work has been published in Phys. Rev. Lett. 92, 247201 (2004), Appl. Phys. Lett. 85, 4085 (2004), and another paper is in press in Phys. Rev. Lett.
2. We have developed a new holographic method for nanoscale magnetic imaging. This method overcomes the phase problem that has been impeding the real space reconstruction of conventional coherent scattering ("speckle") patterns. Our method consists of interfering the scattered intensity from the sample with that of a suitable nanoscale reference hole. A real space image can then be obtained by simple Fourier transform. Our work has been published in Nature 432, 885 (2004).
3. We have explored how fast the magnetization can be switched from one state to the other. Our work has revealed the existence of a speed limit. When the magnetization is switched faster than about 5 picoseconds the switching is no longer deterministic but rather becomes chaotic. Our results have been published in Nature 428, 831 (2004) and Phys. Rev. Lett. 94, 197603 (2005) and the work has received extensive press coverage because of its great technological importance.

Program Impact:

Publications in high profile journals. About 25 invited talks at international conferences. Extensive press coverage, see: <http://www.google.com/search?hl=en&q=data+speed+limit>.

Interactions:

Lawrence Berkeley National Laboratory (A. Scholl, H. Padmore). Seagate Technology (D. Weller)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

J. Stöhr is a member of Scientific Advisory Committees for the synchrotron sources, SOLEIL (Paris) and APS (Argonne).

Personnel Commitments for FY2005 to Nearest +/- 10%:

J. Stöhr 20%, H. C. Siegmann 50%, H. Ohldag 50%, Y. Acremann 30%, W. Schlotter 50%

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$200K **FY04:** \$200K **FY05:** \$200K

FWP and possible subtask under FWP:

SSRL Materials Research, Subtask 3: Scientific and Educational Gateway Program

FWP Number: SCW0035

Program Scope:

The goal of this program is to advance the undergraduate and graduate education of students in the Mexican-American and Mexican communities in science and engineering programs at all levels. The excitement of the scientific opportunities presented by synchrotron-based research is used as a strong stimulus to attract and retain these students. The program includes training in methods of data reduction and analysis as well as developing tools for a collaboratory supporting remote access to instrumentation and data measured at SSRL.

Major Program Achievements (over duration of support):

The program has been quite effective in achieving its primary goal of education in which approximately 50 students from the University of Texas, El Paso (UTEP) in over 130 individual visits to SSRL have participated in the program.: 1) the discovery that alfalfa, which acts as a hyperaccumulator of metals in the soil can form gold nanoparticles in their stems which may have important electronic applications; 2) the understanding of the structure of the stable pigment Maya Blue which is found throughout Meso-America. This understanding has led to the development of a new class of environmentally friendly pigments that are now in precommercialization at UTEP; 3) demonstration that transition metal sulfide hydrodesulfurization nanocatalysts are characterized by carbided surfaces in their stable operating state. This revolutionizes the understanding of the operation of this class of catalysts; 4) In a collaboration with Karen Swyder Lyons of the ONRL, novel fuel cell electrode materials are being studied. Karen has produced fuel cell electrodes using phosphate materials as a support for transition metal catalyst such as Au and Pt. UTEP is synthesizing the materials and characterizing them on the synchrotron. Another important educational aspect is the continuation of an already successful activity; the Stanford-Berkeley Summer School in Applications of Synchrotron Radiation in Physical Science. Anders Nilsson (SSRL) and David Attwood (LBNL) have been the organizers of this annual one-week summer school since 2001, and it will continue for the foreseeable future, with sponsorship provided by the ALS, SSRL. In June 2005 it was organized at SSRL and included 5 students within the Gateway program.

Program Impact:

Many of the students have never been outside of the El Paso/Juarez region and have never seen anything resembling a synchrotron radiation facility. The hardworking, intelligent and enthusiastic Gateway students lack only the opportunity to test their skills against the world's best and discover that they are "up to the task". Dr. Myriam Perez de la Rosa is an example of just one of the many successful Gateway students. During the last three years, Perez has become an up-and-coming, award-winning Latina scientist as a result of her expert training at SSRL. She is currently a postdoctoral fellow in molecular environmental science under the supervision of Dr. John Bargar at SSRL.

Interactions:

R. Chianelli, J. Gardea-Torresdey, G. Lush, N. Pingitore, C. Botez, F. Manchiu, M. Manchiu (UTEP), L. Fuentes Cobas, B. Stec (U. of Mexico, Chihuahua).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2005 to Nearest +/- 10%:

A. Nilsson (5%), A. Mehta (100%), R. Chianelli (8.3%), C. Botez (8.3%), F. Manchiu (8.3%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$336K

FY04: \$336K

FY05: \$336K

FWP and/or subtask Title under FWP:

SSRL Materials Research, Subtask 4: Novel materials and model systems for the study of correlated phenomena (formerly: Nanoscale ordering in complex oxides)

FWP Number: SCW0035

Program Scope:

(1) Obtain fundamental understanding of correlated electron behavior in complex materials by creating and studying simpler systems; (2) Design and synthesis of materials for desired properties and functions; (3) Integration of high end physical characterization in the process of materials development; (4) Act as a national resource for materials development and characterization, and in training students in these fields.

Major Program Achievements (over duration of support):

Role of valence skipping elements in correlated electron behavior: Superconductivity observed in single crystals of TI-doped PbTe. Thermodynamic and transport properties indicate exotic charge Kondo state associated with mixed TI valence (Ti^+ and Ti^{3+}). Implication for pairing mechanism investigated.

Fermi surface reconstruction in CDW compounds: Synthesized crystals of the layered materials RTe_2 and RTe_3 (R = rare earth). Observed CDW formation via TEM and high resolution x-ray diffraction. ARPES measurements reveal large CDW gap ($\sim 400\text{meV}$) for optimally nested regions of Fermi surface, and presence of CDW shadow bands. Quantum oscillations from reconstructed sections of FS.

Origin of bad metal behavior: Further studies of SrRuO_3 confirm that electrical transport in this material cannot be understood in terms of conventional Boltzmann/Drude theory. More recently focus has been on the role of disorder on the electronic properties. Our results show that there are changes in the electronic structure near the Fermi Energy as disorder is increased suggesting some role of correlation.

Charge ordering in CuO: We have successfully synthesized cubic thin films of the normally monoclinic compound CuO using epitaxial growth. The structure and valence of the CuO were confirmed by in situ RHEED, UPS and XPD (x-ray photo diffraction).

High- T_c superconductors: a) Study of disorder effects in Bi2201 and Bi2212: discovered growth method to achieve record T_c of 96K for Bi2212; established new classification scheme of all high- T_c superconductors. b) Established growth method of model high- T_c superconductor Hg1201 yielding crystals 2-3 orders of magnitude larger than previous world record. Resonant Inelastic X-Ray Scattering (RIXS) at the APS on Hg1201 revealed rich structure of charge-transfer excitations.

Program impact:

Materials physics: substantial advances in understanding aspects of correlated electron behavior.

New materials for DOE BES: extensive collaboration based on the materials developed in this program.

Interactions:

D. Basov (UCSD), D. Blank (University of Twente, Netherlands), I. Bosovic, C. Homes (BNL), F. Bridges and Z. Schlesinger (UCSC), S. Brown (UCLA), V. Brouet (LPS Orsay, France), K. Char (Seoul University, Korea), P. Coleman (Rutgers), L. DeGiorgi (ETH, Switzerland), S. Dodge (Simon Fraser University, Canada), S. Dugdale (Bristol, UK), E. M. Forgan, C. Gough (Birmingham, UK), P.M. Grant (EPRI), Z. Islam (APS, ANL), T. Geballe, A. Kapitulnik, S. Kivelson, H. Manoharan, K. A. Moler, N. Ru and Z.-X. Shen (Stanford), L. Klein (Bar Ilan University, Israel), M. Klein (UIUC), A. Mackenzie (St. Andrews, UK), D. van der Marel (Geneva, Switzerland), G. Miller and J. Schmalian (Ames Laboratory), N. P. Ong (Princeton), Rubenhausen (Hamburg, Germany), J. Reiner (Yale), L. Taillefer (Sherbrooke, Canada), M. Toney (SSRL), S. Uchida (Tokyo, Japan), T. Uemura (Columbia), J. Zaanen (Leiden U., Netherlands)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

MRB: 2002 Elected to the Board of Trustees of the Associated Universities Inc.

IRF: 2003 Sloan Research Fellowship; 2004 Terman Fellowship

Personnel Commitments for FY2005 to Nearest +/- 10%:

I. R. Fisher (10%), M. R. Beasley (10%), M. Greven (10%), N. Barisic (10%), L. Litvak (50%), Y. Matsushita (50%), P. SanGiorgio (15%), K.Y. Shin (50%), G. Yu (25%), X. Zhao (50%), X. Zhou (50%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$500k

FY04: \$490k

FY05: \$575k

Laboratory Name: SSRL
B&R Code: KC0202030

FWP and possible subtask under FWP:

SSRL Materials Research, Subtask 5: Nano-scale magnetism in the vortex state of high-Tc cuprates

FWP Number: SCW0035

Program Scope: The project on nano-scale magnetism in the vortex state of high Tc cuprates explores fundamental physical processes which give rise to novel collective phenomena and self-assembled nano-structures resulting from high magnetic fields or complex synthesis processes. The complex nano-structures include antiferromagnetic order inside the vortex cores and checkerboard charge order of the Cooper pairs in high Tc superconductors.

Major Program Achievements (over duration of support):

Theoretical prediction of the antiferromagnetism in the vortex state of high Tc cuprates has been confirmed experimentally by a number of different techniques, including neutron scattering, μ SR, NMR, and in a number of different materials, with both hole and electron doping.

Theoretical prediction of the checkerboard state of the Cooper pairs offers a natural explanation of the 4x4 ordering pattern observed in the STM experiments.

The combined analytical and numerical investigations lead to the construction of the global phase diagram of the high Tc cuprates, which organizes the various competing phases into a common framework. The global phase diagram predicts charge ordering of the Cooper pairs at special rational filling fractions, which have been recently observed in transport experiments.

Program Impact:

Our work has generates great interests within the research community, highlighted by perspective articles in both Science and Nature.

Interactions:

Oakridge National Lab, neutron scattering experiments of PC Dai.

University of Wuerzburg, theory group of Werner Hanke.

Princeton University, STM experiments of Ali Yazdani.

Central Research Institute of Electric Power Industry, Japan, material growth by Yoichi Ando.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

58 Invited talks since 2001.

Personnel Commitments for FY2005 to Nearest +/-10%:

Shoucheng Zhang (10%)

Handong Chen (50%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$94K

FY04: \$94K

FY05: \$95K

FWP and possible subtask under FWP:

SSRL Materials Research, Subtask 6: Nano-scale Phenomena and Their Competitions and Transitions in Complex Materials

(Formerly: Nano-scale Electronic Self-Organization in Complex Oxides)

FWP Number: SCW0035

Program Scope: A collaborative research program focusing on the physics of nanoscale ordering phenomena in complex materials. The objectives of the program include: i) Deeper scientific understanding of correlated electron phenomena. By investigating model systems that address key physical effects found in many complex materials, including competing interactions, coexisting phases and their emergence from the nano-scale to bulk properties; ii) Study of new materials. The heart of this proposal is the collaboration with groups who develop new materials which may be used to answer critical scientific questions, or may be used for future applications; iii) Development of new tools for the study of correlated materials, with on the nano-scale. This approach is unique and involves state of the art facilities. New phenomena will lead to the invention of new ways to investigate them and vice versa. This program will therefore strengthen the wider DOE effort in nano-scale physics in the US; iv) Act as a national resource for the study of the development and characterization of novel materials using novel tools, and in training students and other technical personnel in these fields.

Major Program Achievements (over duration of support):

ARPES: Observation of C60 band structure and its dependence on molecular orientation. Observation of Fermi Surface reconstruction in the CDW state of CeTe_3 .

STM Studies: Built a Novel STM Apparatus for the Study of Complex Materials; Discovery of Coherence peaks 4-period modulation in $\text{Bi}_2\text{Sr}_2\text{CuO}_8$; First understanding of the nature of the gap inhomogeneities in $\text{Bi}_2\text{Sr}_2\text{CuO}_8$.

Local Magnetic Measurements: Demonstrated that vortices pin on antiferromagnetic twin boundaries in $\text{ErNi}_2\text{B}_2\text{C}$ where superconductivity and antiferromagnetism coexist; Demonstrated that a theoretically predicted signature of time-reversal-symmetry breaking superconductivity in Sr_2RuO_4 did not exist.

Other: Demonstrated Piezo-controlled Strain Measurements on Superconductors.

Program Impact:

Power of local measurements has been demonstrated to investigate global properties of strongly correlated materials. Strong interface with the more materials-oriented program of Ian-Fisher and coworkers.

Interactions:

I.R. Fisher, M. Greven, M.R. Beasley, T.H. Geballe, Z.-X. Shen, S. Kivelson, S. Doniach, S. C. Zhang and R. B. Laughlin (Stanford, USA), Zahid Hussain (Princeton, USA), S.G. Louie, M.L. Cohen, LBNL (LBNL), P.C.E. Stamp, G. Sawatzky and R. Harris (UBC, Canada), B. A. Jones, C. P. Lutz, A. S. Heinrich, D. M. Eigler (IBM Almaden, USA), E. J. Heller (Harvard, USA), E. Fradkin (UIUC, USA), John Tranquada (BNL, USA).

Recognitions, Honors and Awards (at least in some part attributable to support under this program):

HM: Undergraduate student Robert McConnell was awarded the Goldwater Scholarship and an NDSEG Graduate Fellowship in 2005 based on his research work.

Personnel Commitments for FY2005 to Nearest +/- 10%:

A. Kapitulnik (10%), H. Manoharan (10%), K. Moler, (10%), A. Fang (50%), A. Geraci (35%), W.L. Yang (50%), W. Meevasana (50%), G. Zeltzer (33%), L. S. Mattos (33%), B. K. Foster (33%), P. Bjornsson (50%), H. Bluhm (50%).

Authorized Budget (BA) for FY03, FY04, FY2005:

FY03: \$500K

FY04: \$490K

FY05: \$575K

FWP and possible subtask under FWP:

SSRL Materials Research, Subtask 7: Nanomagnetism – Spintronics

FWP Number: SCW0035

Program Scope:

This program explores a novel method, called “spin injection”, for manipulating the magnetization on the nanometer length scale and picosecond time scale. The goal is a scientific understanding of the spin injection process that will enable its utilization in technology. Today all magnetic devices depend on the use of conventional magnetic fields generated by current carrying wires to switch the magnetization. This process is relatively slow (1 ns) and inefficient. More efficient and faster switching may be accomplished by injecting a spin polarized current directly into the nanoscale magnetic structure that needs to be switched. The short-range and large fields associated with the injected spins can switch the magnetization in the nanostructure by means of the quantum mechanical exchange interaction. While spin injection has been observed by means of transport measurements, the following scientific challenges remain regarding its understanding and ultimate utilization (i) The current density is too high, near the electromigration limit, (ii) the sign and degree of spin polarization are uncertain, (iii) the optimum relative orientation of spin and magnetization are unknown, and (iv) the dynamics and ultimate speed of the process are not understood. Our program uses the unique capabilities of x-ray microscopy, such as elemental specificity and nanoscale spatial resolution, combined with the picosecond pulse structure of synchrotron radiation to study the spin injection process in real space and real time. It is the only method capable of addressing all four scientific challenges listed above.

Major Program Achievements (over duration of support):

After developing pump-probe time-resolved x-ray imaging techniques (Science 304, 430 (2004)) we have now succeeded in imaging the details of the spin injection process in space and time. While magnetic switching by spin injection had previously been observed in giant magneto-resistance studies following a stepwise change in the injected spin current, the temporal evolution of the nanoscale magnetization distribution during the switching process had remained hidden. Our studies revealed that the switching process is initiated and determined by the lateral motion of a magnetic vortex driven by the spin current. Motion pictures with 200 picosecond time resolution reveal a sub-nanosecond switching process based on the lateral displacement of magnetic vortices, leading to C-like patterns which may decay later into a uniform magnetic state. Our measurements show the fundamental role played by the curled Oersted field which necessarily accompanies the spin injection current. A paper has been submitted to Nature.

Program Impact:

One paper published in Science. About 5 invited talks at international conferences.

Interactions:

B. Clemens, Mat. Sci. Dept., Stanford University; T. Tyliczszak, Lawrence Berkeley National Laboratory.

J. A. Katine and M. Carey, Hitachi Global Storage Systems

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

J. Stöhr is a member of Scientific Advisory Committees for the synchrotron sources, SOLEIL (Paris) and APS (Argonne).

Personnel Commitments for FY2005 to Nearest +/- 10%:

J. Stöhr 20%, Y. Acremann 50%, J. P. Strachan 50%, V. Chembrolu (50%), X. Yu (50%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$100K

FY04: \$200K

FY05: \$200K

Laboratory Name: SSRL
B&R Code: KC0202010

FWP and possible subtask under FWP:

SSRL Materials Research, Subtask 9: LCLS Ultrafast Science Instrumentation (LUSI)

FWP Number: SCW0035

Program Scope:

The goal of this new program is to assess the scientific instrumentation that will be needed to carry out research using the Linac Coherent Light Source (LCLS), now under construction at SLAC. It is expected that this program will mature into a BES-funded Major Item of Equipment (MIE) Project, with project funding starting in FY2007.

Major Program Achievements (over duration of support):

The program was begun midway through FY2005. During 2005, the basic parameters of the initial LCLS research program were organized around five science thrust areas. The instrumentation required to enable these thrust areas was considered, and a conceptual design was crafted for an MIE project which will build four LCLS science instruments. This conceptual design, for the LCLS Ultrafast Science Instruments (LUSI) Project, received approval of its Statement of Mission Need (CD-0) in August, 2005.

Program Impact:

This program is very new, but it draws on years of SSRL involvement with the community of scientists that intend to make use of the LCLS. This community has now been organized into science thrust area teams, with designated spokespeople (the LCLS Science Team Leaders). The program has brought the Team Leaders together on a regular basis, and directed their energy toward defining the optimum instrumentation for carrying out the novel science that will be enabled by LCLS. The program has worked with BES and SLAC to define a mechanism for obtaining this instrumentation.

Interactions:

LCLS Science Team Leaders: N. Berrah, (W. Michigan U), L. DiMauro (Ohio State U), H. Chapman (LLNL), K. Gaffney (SSRL), J. Hajdu (U. Uppsala), P. Heimann (LBNL), J. Larsson (U. Lund), R. Lee (LLNL), K. Ludwig (Boston U), J. Miao (UCLA), D. Reis (U. Michigan), B. Stephenson (ANL), M. Sutton (McGill U)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2005 to Nearest +/- 10%:

J. Arthur 50%

J. Hastings 50%

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$0 **FY04:** \$0 **FY05:** \$1500K

FWP and possible subtask under FWP:

Development and Mechanistic Characterization of Alloy Fuel Cell Catalysts

FWP Number: SCW0040

Program Scope:

One of the main challenges for the Hydrogen Fuel Initiative is to develop cost efficient electrocatalysts with high durability for the generation of electricity in fuel cells. This program is aimed to develop new synchrotron radiation based x-ray diffraction and spectroscopy methods that allow in-situ probing of the intermediates in the catalytic cathode process where both species identification, geometric and electronic structure properties can be fully characterized. The mechanistic understanding provides new insights on how to design new low Pt containing alloy catalyst. In parallel to the fundamental synchrotron work, theory-guided combinatorial synthesis and high throughput electrochemical screening methodologies for fuel cell cathode catalysts are being developed and applied in order to link mechanistic hypotheses and catalyst testing under realistic conditions in high dimensional compositional and process parameter spaces.

Major Program Achievements (over duration of support)

This is a new program that started in August 05.

1. The OH species is currently proposed to be one of the rate limiting reaction intermediates during the oxygen reduction reaction. We have characterized the mixed OH and water phases on Ru(001) and Pt(111) with XPS, XAS and STM under ultrahigh vacuum conditions together with density functional theory calculations. The OH species is lying flat on the surface with the hydrogen atom involved in a weak donating hydrogen bond towards another water molecule. There are important electronic structure rearrangements on the OH group due to interaction with both the substrate and neighboring water molecules that will affect the reactivity.
2. We have studied the reactivity of water to Cu(110) and Cu(111) surfaces at ambient pressures of up to 1 torr using a different pumped electron spectroscopy system. There is a large difference in reactivity between the two surfaces where no adsorption can be found on the close packed 111 surface whereas the open 110 surface interacts strongly with water leading to dissociation into OH and H at room temperature. The presence of OH on the surface dramatically increases the stabilization of adsorbed water. There are changes in the adsorption strength of water by a factor of two due to strong accepting hydrogen bonds from neighboring water molecules.

Program Impact:

This program has the potential to have a large impact on the future Hydrogen Fuel Initiative. Fuel cells are currently considered as the most promising power generation technology for a sustainable energy infrastructure.

Interactions:

A. Nilsson, M. Toney, H. Ogasawara (SSRL), P. Strasser (University of Houston), Lars Pettersson, Michael Odelius, Lars Åke Näslund, Klas Andersson, Theanne Schiros (Stockholm University).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Two invited talks at international conferences

Personnel Commitments for FY2005 to Nearest +/- 10%:

A. Nilsson 10%, H. Ogasawara 100 %, Mike Toney 10% (SSRL), Peter Strasser 10% (UH)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$0K **FY04:** \$0K **FY05:** \$600K

FWP and possible subtask under FWP:

Behavior of Charges, Excitons and Plasmons at Organic/Inorganic Interfaces

FWP Number: SCW0034

Program Scope:

Exciton transport and molecular wavefunction coupling to metal electrodes on the molecular level (~1 nm). Exciton and charge transport within semiconducting polymer films close to metallic electrodes or dielectric films (5-100 nm). Exciton coupling to surface plasmon waves on metal surfaces within the 10-500 nm range. Collectively, these measurements will provide a better overall understanding of the behavior and importance of charges, excitons and plasmons within electrically active organic-inorganics than would be possible from a single study alone.

Major Program Achievements (over duration of support):

Charge transport in semiconducting polymers: Used synchrotron x-ray diffraction to show that charge carrier mobility is highest in polymer transistors when crystals nucleate off of the gate dielectric. When the crystals do not nucleate off of the dielectric, they are not all aligned with each other and the insulating side chains prevent charge hopping from one grain to another.

Exciton transport in semiconducting polymers: Showed that many exciton diffusion lengths reported in the literature are overestimated due to not accounting for optical interference effects. The diffusion length in most polymers used for solar cells is 3-6 nm. Exciton harvesting can be improved by choosing donor and acceptor polymers that enable Förster resonance energy transfer.

Transport at the molecular scale: Developed a new method to softly contact molecular monolayers with a large area (>mm²) top metal electrode without shorting or damaging the molecular monolayer. Demonstrated tunneling behavior for alkane carbon chains, and molecular switching behavior for rotaxane molecules within large-area junctions. Developed surface plasmon spectroscopy apparatus and for the first time measured the optical absorption spectrum of a rotaxane monolayer between metal electrodes.

Radiative decay engineering: Performed simulations of the emission enhancement for a dipole emitter placed in a subwavelength metal optical cavity. Optimized the cavity dimensions to realize a light source with an almost omnidirectional emission. Fabricated and tested an organic light emitter for which thin Au films formed both the optical cavity and the electrical contacts.

Program impact:

The understanding gained from this research will enable the fabrication of more efficient organic solar cells, the extraction of more light from light emitting diodes that can be used for displays or solid-state lighting, and the fabrication of better molecular electronics devices and optical switches.

Interactions:

U.C. Berkeley: Chemistry (J. Fréchet), Stanford University: Chemical Engineering (Z. Bao)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

M.D. McGehee was chosen to speak at the 2006 National Academy of Engineer's Frontiers of Engineering Meeting and had 7 invited talks this year related to this project. M.L. Brongersma had 11 invited talks and 1 invited tutorial related to this project. N.A. Melosh has given 1 invited talk, and was part of a Gordon Research Conference on this subject.

Personnel Commitments for FY2005 to Nearest +/- 10%:

N.A. Melosh 5 %, M.L. Brongersma, 5 %, M.D. McGehee, 5 %, S. Scully 50 %, J. Fabbri 50 %, J. Liu 50 %

Authorized Budget (BA) for FY03, FY04, FY05:

FY03: \$0K

FY04: \$0K

FY05: \$275K